

Kohn-Sham Kinetic Energy Density in the Nuclear and Asymptotic Regions: Deviations from the Von Weizsäcker Behavior and Applications to Density Functionals

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(Dated: November 17, 2014)

We show that the Kohn-Sham positive-definite kinetic energy (KE) density significantly differs from the von Weizsäcker (VW) one at the nuclear cusp as well as in the asymptotic region. At the nuclear cusp, the VW functional is shown to be linear and the contribution of p -type orbitals to the KE density is theoretically derived and numerically demonstrated in the limit of infinite nuclear charge, as well in the semiclassical limit of neutral large atoms. In the latter case, it reaches 12% of the KE density. In the asymptotic region we find new exact constraints for meta Generalized Gradient Approximation (meta-GGA) exchange functionals: with an exchange enhancement factor proportional to $\sqrt{\alpha}$, where α is the common meta-GGA ingredient, both the exchange energy density and the potential are proportional to the exact ones. In addition, this describes exactly the large-gradient limit of quasi-two dimensional systems.

PACS numbers: 71.10.Ca, 71.15.Mb, 71.45.Gm

Ground-state density functional theory (DFT) [1–4] can be considered the most used method in electronic calculations of quantum chemistry and condensed matter physics. DFT is in principle an exact approach to electronic structure theory. However, in practice the exchange-correlation (XC) and, in the case of orbital-free DFT [5], the non-interacting kinetic energy (KE) functionals need to be approximated. The construction of approximate XC and KE functionals is thus an active field within DFT [6–8].

The Kohn-Sham (KS) positive-definite KE density $\tau^{\text{KS}} = (1/2) \sum_i |\nabla \phi_i|^2$, where ϕ_i are the occupied KS orbitals, is of course a key quantity for KE functionals but plays a major role also in meta-Generalized Gradient Approximation (meta-GGA) XC energy functionals, which are recently attracting strong interest [9–13]. The properties of τ^{KS} have been studied since long [3, 4], suggesting that it approaches the von Weizsäcker (VW) kinetic energy density functional [14], $\tau^W[\rho] = |\nabla \rho|^2/(8\rho)$, both in the cusp [4, 15–19] and in the asymptotic regions [4, 15, 18, 20–22]. These conditions have been used in the derivation of approximated KE functionals [19–22].

Concerning the nuclear region, it was more recently shown that τ^{KS} differs from τ^W at the nuclear cusp [23]. In this work we will present a new derivation of the KE at the nuclear cusp which is based on the linearity of the VW functional at the cusp. Moreover, we will derive the semiclassical limit for the exact KE density as well as the limit for isoelectronic series at the nuclear cusp.

Concerning the asymptotic region of atoms it has been previously observed [24–26] that τ^{KS} can have different asymptotic properties from τ^W , if the outer-valence electrons are not of s -type. In this work, we will show an exact asymptotic expression for the Pauli excess KE density [3, 16, 27] $\tau^{\text{P}} = \tau^{\text{KS}} - \tau^W$, and use it to derive

a new constraint for the asymptotic behavior of meta-GGA exchange functionals. This is an almost unexplored topic since, so far, most of the effort has been put into the investigation of the asymptotic properties of GGA functionals. However, the latter cannot display simultaneously the correct asymptotic behavior for both the exchange energy per particle ($\epsilon_x \rightarrow -1/(2r)$) and the exchange potential $v_x \rightarrow -1/r$ [28, 29]. Thus, e.g., the Becke exchange [30] has an exact asymptotic behavior for ϵ_x , but v_x is proportional to $-1/r^2$ [31]. On the other hand, a recent functional [29] with the correct $v_x \rightarrow -1/r$ has been developed, but it has a nonphysical ϵ_x . In this letter we will show instead that the aforementioned constraints can be merged at the meta-GGA level.

We start considering a closed-shell system in an arbitrary central spherical potential $V(r)$ (e.g. atoms, jellium spheres, ...). A given shell is characterized by n, l quantum number and all orbitals with $m = -l, \dots, l$ contribute to shell density ρ_{nl} . The positive-definite KE density of the shell can be written as [32, 33]:

$$\tau_{nl}^{\text{KS}} = \tau^W[\rho_{nl}] + \frac{l(l+1)}{2} \frac{\rho_{nl}}{r^2}. \quad (1)$$

The total KS positive-defined KE density is $\tau^{\text{KS}} = \sum_{nl} \tau_{nl}^{\text{KS}}$. Note that this simple formula does not apply to the non-linear VW functional, since $\tau^W[\rho] \neq \sum_{nl} \tau^W[\rho_{nl}]$. Eq. (1) is the starting equation for this work and it is valid *everywhere* in the space, for any shell and any central potential. In the following we consider two limits for Eq. (1), namely $r \rightarrow 0$ and $r \rightarrow \infty$.

When $r \rightarrow 0$ we have that (for $l \geq 1$) $\rho_{nl} \rightarrow A_{nl} r^{2l}$, where A_{nl} is a constant. Thus, the second term on the right-hand-side of Eq. (1) is A_{n1} for $l = 1$ and vanishes

for $l \geq 2$. For the VW term at $r = 0$ we have for $l = 1$

$$\tau^W[\rho_{n1}](0) = \frac{1}{8} \frac{(2A_{n1}r)^2}{A_{n1}r^2} = \frac{1}{2} A_{n1}, \quad (2)$$

whereas $\tau^W[\rho_{n,l}](0)$ vanishes for $l \geq 2$ and for $l = 0$ it depends on the central potential. Summarizing, we have

$$\tau_{nl}^{\text{KS}}(0) = \begin{cases} \tau^W[\rho_{n0}](0) & \text{for } l = 0 \\ \frac{1}{2} A_{n1} + A_{n1} = 3\tau^W[\rho_{n1}](0) & \text{for } l = 1 \\ 0 & \text{for } l \geq 2 \end{cases}. \quad (3)$$

To stress the significance of this result we consider the special case of a central potential with a leading term $-Z/r$ near the core. In this case the Kato theorem [34] holds for any spherical shell [35], i.e. $\left. \frac{\partial \rho_{n0}(r)}{\partial r} \right|_{r=0} = -2Z\rho_{n0}(0)$. Therefore

$$\tau^W[\rho_{n0}](0) = \frac{1}{8} \frac{[-2Z\rho_{n0}(0)]^2}{\rho_{n0}(0)} = \frac{Z^2}{2} \rho_{n0}(0). \quad (4)$$

The main finding here is that Eqs. (4) and (2) are *linear* in $\rho_{n0}(0)$ and A_{n1} , respectively. Thus we have:

$$\tau^W[\rho_s](r) = \sum_{n=1}^{N_s} \tau^W[\rho_{n0}](r) \quad \text{for } r = 0, \quad (5)$$

$$\tau^W[\rho_p](r) = \sum_{n=2}^{N_p} \tau^W[\rho_{n1}](r) \quad \text{for } r = 0, \quad (6)$$

where $\rho_s = \sum_{n=1}^{N_s} \rho_{n0}$ and $\rho_p = \sum_{n=2}^{N_p} \rho_{n1}$, with N_s and N_p being the maximum principal quantum numbers for occupied s -type and p -type shells respectively. We underline that the linearity of the VW functional is valid only at the nuclear position. This is shown in Fig. 1 where both sides of Eq. (5) are reported versus the radial distance for, e.g., the Argon atom. For the corresponding plot of both sides of Eq. (6), see Ref. [33]. All calculations in this work have been performed with a numerical atomic code using non-relativistic exact-exchange (EXX)[36].

Combining Eqs. (5) and (6) with Eq. (3) we have for the total positive-defined KE density at the origin:

$$\tau^{\text{KS}}(0) = \sum_{nl} \tau_{nl}^{\text{KS}}(0) = \tau^W[\rho_s](0) + 3\tau^W[\rho_p](0). \quad (7)$$

Hence, the exact positive-defined KE density at the origin depends on both s -type and p -type contributions. A numerical evidence of the validity of Eq. (7) for, e.g., the Argon atom is given in Fig. 1.

In order to estimate the effective role of the p -type orbitals on real calculations we consider all neutral closed-shell noble atoms up to $N_e = Z = 2022$ (i.e. up to 21 p -shells; here and hereafter N_e is the number of electrons

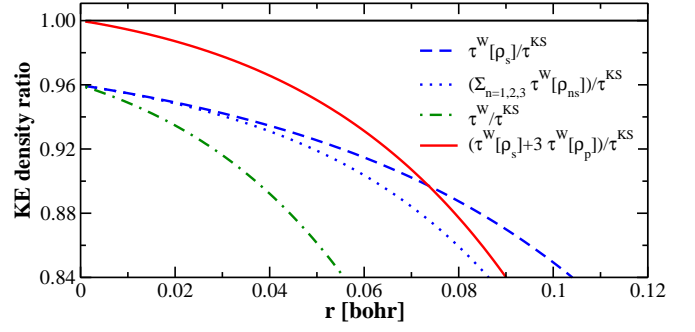


FIG. 1: Ratios of different kinetic energy (KE) densities to the exact KE (τ^{KS}) for the Argon atom, near the nucleus. The dashed and dotted lines coincide at $r = 0$, showing the linearity of the VW functional for s -shells. The red solid line approaches 1 at $r = 0$ showing the validity of Eq. (7).

and Z is the nuclear charge). In Fig. 2a we report the quantity

$$\Delta^{\text{EXX}} = \frac{3\tau^W[\rho_p](0)}{\tau(0)} = \frac{3\tau^W[\rho_p](0)}{\tau^W[\rho_s](0) + 3\tau^W[\rho_p](0)}, \quad (8)$$

as a function of $N_e^{-1/3}$. Fig. 2a shows that for the small-

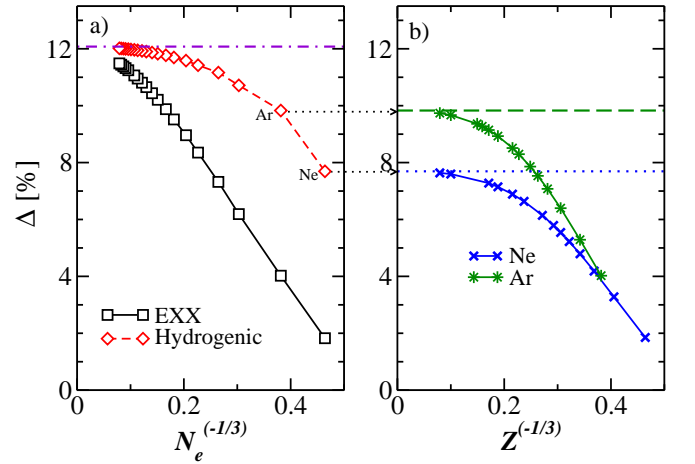


FIG. 2: Relative contribution (Δ in percent) of p -shells to the positive-defined KS kinetic energy density at the nuclear cusp for: a) neutral noble-gas atoms up to $N_e = 2022$ as a function of $N_e^{-1/3}$. Results using EXX and hydrogenic orbitals are shown. The horizontal dashed-line represents the theoretical limit, see Eq. (11). b) Ne and Ar isoelectronic series with EXX orbitals up to $Z = 2000$. The horizontal dashed-lines represent the theoretical limits, see Eq. (10).

est atom considered (i.e. Neon) the role of p -type orbitals is quite small (1.8%). However, it increases almost linearly with $N_e^{-1/3}$ and for Radon Δ^{EXX} is already above 8%. To investigate the semiclassical limit for $N_e \rightarrow \infty$ we further consider hydrogenic orbitals [38]. After some algebra the following relations are obtained:

$$\tau^W[\rho_{n0}](0) = \frac{Z^5}{\pi n^3}; \quad \tau^W[\rho_{n1}](0) = \frac{(n^2 - 1)Z^5}{3\pi n^5}, \quad (9)$$

$$\Delta^{\text{HYD}}[N_e] = \frac{\sum_{n=2}^N (\frac{1}{n^3} - \frac{1}{n^5})}{\sum_{n=1}^N \frac{1}{n^3} + \sum_{n=2}^N (\frac{1}{n^3} - \frac{1}{n^5})}, \quad (10)$$

where N is the number of filled shells ($N = N_s = N_p$ for noble atoms) and the total number of electron is $N_e = (N^3 + 6N^2 + 11N - 6)/6$ if N is odd and $N_e = (N^3 + 6N^2 + 14N)/6$ otherwise. A plot of Δ^{HYD} as a function of $N_e^{-1/3}$ is reported Fig. 2a. For small atoms Δ^{HYD} differs quite significantly from Δ^{EXX} because, due to screening effects, EXX orbitals are rather different from hydrogenic orbitals. Nevertheless, differences reduce for larger atoms and both quantities converge to similar results for large N_e values. Using the hydrogenic orbitals the limit $N_e \rightarrow \infty$ can be computed exactly as

$$\lim_{N_e \rightarrow \infty} \Delta^{\text{HYD}}[N_e] = \frac{\zeta(3) - \zeta(5)}{2\zeta(3) - \zeta(5)} = 0.12078, \quad (11)$$

where $\zeta(x)$ is the Riemann function. Thus, in the semi-classical limit, the p -type orbitals contribute to τ^{KS} at the origin by 12%, clearly showing that the VW functional can be quite inaccurate in the cusp region.

Then we consider positively charged noble atoms. In Fig. 2b we report Δ^{EXX} for Ne and Ar isoelectronic series, as a function of $Z^{-1/3}$. Also in these cases, in the limit for $Z \rightarrow \infty$ the hydrogenic orbitals model becomes exact as there are no screening effects on the nuclear charge for any shell. Thus the $Z \rightarrow \infty$ limit can be obtained from Eq. (10): for Neon ($N = 2$, $N_e = 10$) we obtain $\Delta^{\text{HYD}} = 1/13$, for Argon ($N = 3$, $N_e = 18$) $\Delta^{\text{HYD}} \approx 0.983$. These values are shown as horizontal lines in Fig. 2b, and are correctly approached by calculated values of Δ^{EXX} .

We now turn to analyze Eq. (1) in the limit $r \rightarrow \infty$. In the asymptotic region only the outer shell (with $n = \tilde{n}$ and $l = \tilde{l}$) contributes to the density [39], i.e. $\rho \rightarrow \tilde{\rho} = \rho_{\tilde{n}\tilde{l}}$ (with a \sim we indicate asymptotic quantities). From Eq. (1) the asymptotic expression for τ^{P} is obtained:

$$\tau^{\text{P}} = \tau^{\text{KS}} - \tau^{\text{W}} \xrightarrow{r \rightarrow \infty} \tau_{\tilde{n}\tilde{l}}^{\text{KS}} - \tilde{\tau}^{\text{W}} = \frac{\tilde{l}(\tilde{l}+1)}{2} \frac{\tilde{\rho}}{r^2} = \tilde{\tau}^{\text{P}}. \quad (12)$$

where we used that $\tau^{\text{W}} \rightarrow \tilde{\tau}^{\text{W}} = \tau^{\text{W}}[\tilde{\rho}]$. When $\tilde{l} = 0$, i.e. for s -type outer-valence electrons, Eq. (12) indicates that τ^{KS} asymptotically approaches τ^{W} , exactly [4, 15, 18, 20–22]. On the other hand, for systems with degenerate outer shells (p -, d -, ..., -type electrons), e.g. all atoms but groups I or II, $\tilde{\tau}^{\text{P}}$ is not zero and decays with the same exponential decay of the density: thus it is very important in the near and middle asymptotic region [33]. Eq. (12) is asymptotically exact, in the sense that no additional terms with different radial powers are present, and it is valid for any spherical system, clarifying and generalizing previous observations [24–26].

We then consider the following exchange energy density per particle

$$\epsilon_x = \epsilon_x^{\text{LDA}} F_x \quad \text{with} \quad F_x = A \frac{8\pi}{\sqrt{15}} \sqrt{\alpha}, \quad (13)$$

where $\epsilon_x^{\text{LDA}} = -C_x \rho^{1/3}$ (with $C_x = (3/4)(3/\pi)^{1/3}$) is the exchange energy per particle in the local density approximation, F_x is the exchange enhancement factor and $\alpha = (\tau^{\text{KS}} - \tau^{\text{W}})/\tau^{\text{TF}}$ is the well known meta-GGA ingredient [40], with $\tau^{\text{TF}} = C_s \rho^{5/3}$ (with $C_s = (3/10)(3\pi^2)^{2/3}$) being the Thomas-Fermi KE density [41]; A is a positive constant (with the factor $8\pi/\sqrt{15} = \sqrt{8C_s}/C_x$ included for simplicity; see below). The expression in Eq. (13), i.e. an enhancement factor (F_x) proportional to $\sqrt{\alpha}$ is not new. It was derived in Ref. [42] with $A \approx 0.3$ to describe exactly the exchange in the large-gradient limit of quasi-two dimensional (quasi-2D) systems. Previous investigations of α were instead mostly related to the description of bonds [26]. Here we consider a completely different physics and study the tail region of atoms.

We rewrite Eq. (13) as

$$\epsilon_x = -AC_x \frac{8\pi}{\sqrt{15}} \sqrt{\frac{\tau^{\text{KS}} - (\nabla\rho)^2/(8\rho)}{\rho C_s}} = (-A) \frac{\Theta}{\rho}, \quad (14)$$

with $\Theta = \sqrt{8\tau^{\text{KS}}\rho - (\nabla\rho)^2}$. From Eq. (12) we have that $\Theta \rightarrow 2\sqrt{\tilde{l}(\tilde{l}+1)}(\tilde{\rho}/r)$. Thus

$$\epsilon_x \rightarrow 2(-A)\sqrt{\tilde{l}(\tilde{l}+1)}\frac{1}{r}, \quad (15)$$

and the the exact asymptotic decay ($\epsilon_x \rightarrow -1/(2r)$) is obtained if

$$A = A' = 1/\left(4\sqrt{\tilde{l}(\tilde{l}+1)}\right). \quad (16)$$

Concerning the exchange potential, we consider the generalized Kohn-Sham framework to write [43]

$$\begin{aligned} v_x \phi_i &= \left[\frac{\partial(\rho\epsilon_x)}{\partial\rho} - \nabla \frac{\partial(\rho\epsilon_x)}{\partial\nabla\rho} \right] \phi_i - \frac{1}{2} \nabla \left(\frac{\partial(\rho\epsilon_x)}{\partial\tau^{\text{KS}}} \right) \nabla \phi_i \\ &\quad - \frac{1}{2} \frac{\partial(\rho\epsilon_x)}{\partial\tau^{\text{KS}}} \nabla^2 \phi_i \\ &= \frac{\partial(\rho\epsilon_x)}{\partial\rho} \phi_i - \nabla \cdot \left[\frac{\partial(\rho\epsilon_x)}{\partial\nabla\rho} \phi_i + \frac{1}{2} \frac{\partial(\rho\epsilon_x)}{\partial\tau^{\text{KS}}} \nabla \phi_i \right] \\ &\quad + \left(\frac{\partial(\rho\epsilon_x)}{\partial\nabla\rho} \right) \cdot \nabla \phi_i. \end{aligned} \quad (17)$$

As first step we compute the partial derivatives of $\rho\epsilon_x = (-A)\Theta$ with respect ρ , $\nabla\rho$, τ^{KS} :

$$\begin{aligned} \frac{\partial(\rho\epsilon_x)}{\partial\rho} &= (-A) \frac{4\tau^{\text{KS}}}{\Theta} = (-A) \frac{\Theta}{2\rho} + \frac{\partial(\rho\epsilon_x)}{\partial\tau^{\text{KS}}} \frac{(\nabla\rho)}{4\rho} \frac{(\nabla\rho)}{2\rho} \\ \frac{\partial(\rho\epsilon_x)}{\partial\nabla\rho} &= (-A) \frac{(\nabla\rho)}{\Theta} = \frac{\partial(\rho\epsilon_x)}{\partial\tau^{\text{KS}}} \frac{(\nabla\rho)}{4\rho} \\ \frac{\partial(\rho\epsilon_x)}{\partial\tau^{\text{KS}}} &= (-A) \frac{4\rho}{\Theta}. \end{aligned} \quad (18)$$

Interestingly Eq. (18) shows that the exchange energy per particle of Eq. (13) possesses the desirable property

that $\partial(\rho\epsilon_x)/\partial\tau^{\text{KS}} < 0$, which was shown to be essential for an accurate description of the optical properties of semiconductors at the meta-GGA level [9]. In contrast, no other non-empirical meta-GGA functional recovers this condition. Inserting the derivatives into Eq. (17) we find

$$v_x\phi_i = (-A)\frac{\Theta}{2\rho}\phi_i - \nabla \cdot \left[\frac{\partial(\rho\epsilon_x)}{\partial\tau^{\text{KS}}} \left\{ -\frac{(\nabla\rho)}{4\rho}\phi_i + \frac{1}{2}\nabla\phi_i \right\} \right] + \frac{\partial(\rho\epsilon_x)}{\partial\tau^{\text{KS}}} \frac{(\nabla\rho)}{4\rho} \left\{ \frac{(\nabla\rho)}{2\rho}\phi_i - \nabla\phi_i \right\}. \quad (19)$$

This expression clearly depends on the considered orbital ϕ_i . For the asymptotic properties we have to consider the highest occupied orbital $\phi_i = \phi_H$: in this case the asymptotic density is $\tilde{\rho} = f\phi_H^2$ and the terms in curly braces in Eq. (19) vanish identically. Thus, we finally obtain

$$v_x\phi_H = (-A)\frac{\theta}{2\rho}\phi_H \rightarrow A\sqrt{\tilde{l}(\tilde{l}+1)}\frac{1}{r}\phi_H, \quad (20)$$

that recovers the exact asymptotic decay ($v_x \rightarrow -1/r$) if

$$A = A'' = 1/\left(\sqrt{\tilde{l}(\tilde{l}+1)}\right). \quad (21)$$

Despite the two constant A' and A'' in Eqs. (16) and (21) differ by a factor of 4, the here proposed expression for ϵ_x (Eq. (13)) yields asymptotic properties proportional to the exact ones for *both* the exchange energy density and the exchange potential. This is a strong improvement with respect to current meta-GGAs where ϵ_x and v_x decay exponentially and GGA functionals where either ϵ_x or v_x can have the exact properties.

To validate the previous analytic results we consider in Fig. 3 the comparison of ϵ_x and v_x obtained from Eq. (13) for p - and d -type closed-shell atoms (i.e. Ne and Zn^{2+}) and for a jellium sphere with 34 electrons and $r_s=2.07$ (having a f -type outer shell). Results from Eq. (13) are compared to EXX and standard GGAs.

The numerical results confirm that, unlike other semilocal approximations (e.g. PBE [37]), the simple expression in Eq. (13) yields the correct asymptotic behavior for ϵ_x (i.e. $-1/(2r)$). Fig. 3 also shows that Eq. (13) is also in better agreement with EXX than the B88 exchange [30]; the latter, in fact, approaches $-1/(2r)$ only at very large distances. For the exchange potential Eq. (13) and Eq. (21) give a $-1/r$ behavior, whereas PBE and B88 decay much faster (exponentially and proportional to $-1/r^2$, respectively).

We thus propose that the expression in Eq. (13) can be a powerful tool in the development of meta-GGA exchange functionals. Clearly completely new functional forms need to be developed in order to satisfy Eq. (13) in the asymptotic region. Moreover, additional work needs to be done to take into account the l -dependence in

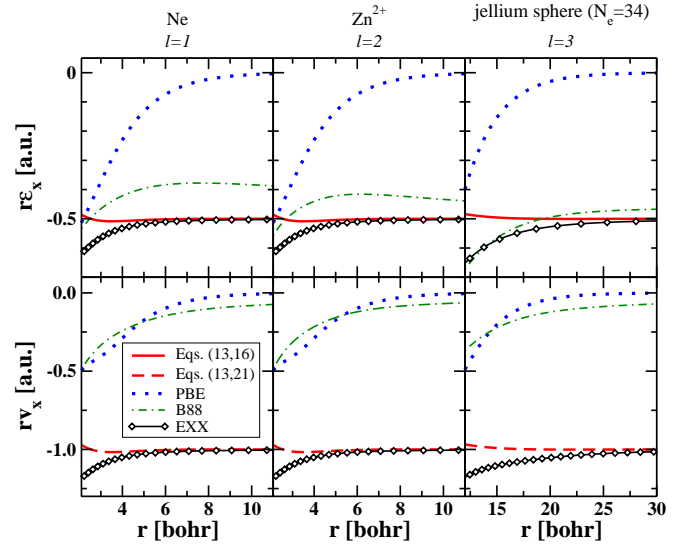


FIG. 3: Exchange energy per particle ϵ_x (upper panels) and exchange potential v_x (lower panels), multiplied by the radial distance r , from different approaches and for Ne, Zn^{2+} , and a jellium sphere with 34 electrons, having p -, d -, and f -type outer shell, respectively.

Eqs. (16) and (21) as well as investigations for molecules, where the anisotropy of τ^{KS} can also play a role [44] and the KS exchange potential can show asymptotic barrier-well structures [45].

Finally, Eqs. (12) can be used to derive an asymptotically correct expression for the non-interacting KE at the GGA level of theory, i.e. $\tau = \tau^{\text{TF}}F_s(s)$, where $F_s(s)$ is the KE enhancement factor which depends on the reduced gradient $s = |\nabla\rho|/(2(3\pi^2)^{1/3}\rho^{4/3})$. In fact, recalling that for an exponential density the expression $\rho\epsilon_x^{LDA}(4\pi/9)(s/\ln(s))$ decays as $-\rho/(2r)$ [6, 30] then $(20/27)\tau^{\text{TF}}(s/(\ln(s))^2)$ will decay as $-\rho/(2r^2)$. Thus

$$F_s \rightarrow \frac{5}{3}s^2 \left(1 + \frac{4}{9} \frac{\tilde{l}(\tilde{l}+1)}{\ln^2(s)} \right), \quad (22)$$

represents a new exact constraint for GGA kinetic energy functionals in the asymptotic region.

In conclusion, from a simple analytic expression (Eq. (1)) we have shown that: i) p -type electrons largely contribute to the positive-defined KE density at the nucleus. This property has been derived considering the linearity of the VW functional at the cusp. For the Neon atom (with only one p -shell) in the limit of infinite nuclear charge, $\Delta \approx 8\%$; in the semiclassical limit of neutral large atoms, Δ reaches 12%. Thus the physics of the KE density near the nucleus region has fully non-local features (i.e. ρ_p is a non-local functional of ρ), which can be hardly captured by semilocal ingredients.

ii) The asymptotic expression of the Pauli excess KE density has been used to construct a new meta-GGA exchange functional: a simple enhancement factor term

proportional to $\sqrt{\alpha}$ can well describe the asymptotic behavior of ϵ_x and v_x , as well as the quasi-2D density regime. This is an important achievement of the meta-GGA level of theory, with respect to the GGA one. In fact, at the GGA level, the infinite barrier model quasi-2D limit can be described only if the GGA exchange enhancement factor decays as $F_x \rightarrow s^{-1/2}$ [46], the asymptotic behavior of ϵ_x can be described only if $F_x \rightarrow s/\ln(s)$ [30], while the asymptotic behavior of v_x can be described only if F_x diverges at least as s [29]. Thus, important future developments in the construction of accurate non-empirical meta-GGA DFT functionals can be foreseen. Nevertheless, we remark that the inclusion of the present results into a practical tool still requires additional effort, in particular for the development of an appropriate and flexible enough meta-GGA functional form in order to correctly describe asymptotic and quasi-2D regimes. Finally, Eq. 22 is also relevant for future development of approximated KE functionals with improved asymptotic behavior.

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